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Archaeologic analogues: Microstructural changes by natural ageing in carbon steels

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Abstract

When discussing the container material for highly active radionuclear waste, carbon steel is one of the materials most frequently proposed by the international scientific community. Evidently, security with respect to the container behaviour into deep geological deposits is fundamental. Among other parameters, knowledge about material mechanical properties is essential when designing the container. Time ageing of carbon steel, apart from possible alterations of the chemical composition (e.g. corrosion) involves important microstructural changes, at the scale of centuries and millenniums. The latter may cause variations of the mechanical properties of carbon steel storage containers, with the corresponding risk of possible leakage. In order to properly estimate such risk and to adjust the corresponding mathematical models to reality, the microstructural changes observed in this study on archaeologic samples are evaluated, comparing ancient and modern steels of similar chemical composition and fabrication processes.

1. Introduction

Archaeologic analogues have potential to provide valuable information about the physico-chemical and mechanical behaviour of metallic containers destined for storage of highly active radionuclear waste. These containers have to be secure during thousands of years, when definitely confined to deep geological deposits. Among other proposals, carbon steel presents one of the most accepted solutions when designing this kind of containers. The contribution of archaeologic carbon steel analogues in this field has three different aspects: corrosion rate associated to the geo-chemical properties of the ground surroundings, microstructural changes by ageing during large periods of time and diffusion models for different elements through the oxide layer present in such samples [1–4]. This investigation is focused on the quantification of microstructural changes in archaeologic carbon steel samples caused by ageing during centuries and millenniums.

The changes on mechanical properties can be associated to modifications in the microstructure of the steel, which have to be taken into account when designing containers for deep geological deposits. Based on a

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Table 1
Description of the archaeologic sites, their geographic localisation, type of sample extracted and dating

Site	Localization	Dating	Type of sample	Description
Roman thermal spring, Republic and Imperial era [3,4]	Cerro Muriano (Córdoba)	1st century A.D. 1st century B.C.	Well conserved steel nail	12 cm long nail with pinhead
Roman hermitage [3,4]	Mijangos	5th century A.D.	Well conserved steel nail	10 cm long nail with pinhead
Mosque of Córdoba (roof) Caliphal era [5]	Córdoba	10th century A.D.	Well conserved steel nail	15 cm long nail with pinhead

metallographic study of the various archaeologic samples under investigation, there is evidence of a change in the initial morphology of the carbon steel microstructure because of a natural ageing process. Though the mechanism of these processes is still not very well understood [4], it is relatively easy to detect modifications in the microcomponents of carbon steels.

In the present research, we have compared ancient steel structures with equivalent structures of nowadays manufactured steels. In all cases, we have studied hypoeutectoid carbon steels with approximately 0.15 wt% carbon content.

Ancient steels have suffered from thermal treatment as a result from the hot forging manufacturing process and normalisation. Modern steels are manufactured by hot drawing and normalizing.

The selection of all archaeologic samples has been made attending to the chronologic reliability of the archaeological deposits they belong and the extension of metallic areas without any trace of corrosion. Each archaeologic sample stems from excavation sites of the Iberian Peninsula.

Fig. 1. Schematic map of the Iberian Peninsula, indicating the geographical location of the different archaeologic sites, where the investigated samples were extracted.

All archaeologic pieces under study have a high reliability respecting their chronology. They have been extracted from safe and trustworthy layers in systematic archaeologic excavations and restoration works (Table 1). Due to intense prehistory and history at the Iberian Peninsula, and, therefore, to its richness in archaeologic artefacts all of the studied archaeologic sites belong to the Peninsula, chronology varying from millenniums to hundreds of years (Fig. 1). The age of different layers of the excavated sites is accurately defined by relevant archaeologic studies. This is important when trying to establish a quantification of structural changes suffered from the samples over the time, using the variation of mechanical properties as an indicator.

2. Experimental

The number of studied samples was high, but, in order to simplify the conclusion of the study, only the clearer structures, showing differences with modern similarly manufactured steels, will be discussed.

The samples belong to three different excavation sites (Table 1). One is the Roman thermal spring of Cerro Muriano, Cordoba, which belongs to the Republic and High Empire period, more precisely, during the regency of the emperors Augustus and Tiberius. The excavation is located about 16 km north of the city of Cordoba, formerly known as Colonia Patricia, in the centre of the mountain range Sierra Morena. The site is still under excavation, most of the recent findings are exhibited at the Copper Museum of Cerro Muriano [3,4].

The second site is the hermitage Santa Maria de Mijangos, which belongs to the late Roman empire and Visigotic period, erected approximately during the 5th century A.D. The building is placed in the neighbourhood of Mijangos, part of the city of Cuesta Urria, North of the actual Burgos province. The complex was destroyed during the 9th and 10th century. The sample investigated from this site belongs to the layer of the late Roman empire and is dated to the 5th century. The ruins of the hermitage are nowadays opened for the public, part of the findings can be seen at the site itself and others are exhibited in the Archaeological Museum of Burgos [3,4].

The famous mosque of Cordoba is origin of another sample investigated in this study. The construction of this complex began under the Arabic dominion of Spain (Al-Andalus) by the family of the Omeyas, in particular by AbderrahmanI from 785 to 786. The last enlargement was realised during the regency of vizier Almanzor in 987. The sample was extracted during a restoration campaign from noble and tilled wood, part of the roof structure of the main nave of the mosque [5]. This nave belongs to the enlargement realised during the regency of Caliph AlhaquemII, the son of AbderrahmanIII, during the period from 961 to 976 A.D. [6].

The modern steel samples used as reference are:

(a) ASTM 1020, a hypoeutectoid steel, hot-rolled and normalized. Carbon content: 0.20 wt% and manganese content: 0.40 wt%.
(b) Steel sample was produced for this investigation by Acerinox S.A. [7], hot-rolled and normalized. The sample contains (in wt%): 1.85% C, 0.03% Si, 0.11% Mn, 0.21% P, 0.15% Cr, 0.06% Ni and 0.04% Cu.

In general, the ancient hypoeutectoid steel samples under investigation show a very similar composition, with values of 0.15% C, 0.4% Si, 0.4% Mn, <0.01% S and <0.001% P in total mass. Some samples may present certain heterogeneity due to the common reuse of oddments from different provenance when fabricating a new product.

The chemical composition of the ancient hypereutectoid steel was determined to be: 1.65% C, 0.4% Mn, 0.4% Si, <0.01% S and <0.001% P in total mass [3,4]. All the selected samples were hot-forged and then cooled down in air (normalized).

In order to avoid irreversible damage of the archaeological samples, they were carefully extracted from its matrix, then embedded in polyester resin and conventionally grinded and polished. The sample surface was then treated for 45 s with 15% of nitric acid in ethylic solution to examine its metallic structure using scanning electron microscopy (SEM). The ancient steel samples were additionally gold sputtered for this purpose.

3. Results and discussion

The pearlite phase of a hypo or hypereutectoid hot-rolled normalized steel consists of a laminar structure of cementite and ferrite, as demonstrated in Figs. 2 and 3. The cementite lamellae exhibit, as shown in Fig. 4, a somewhat sinuous (wavy) morphology. In the

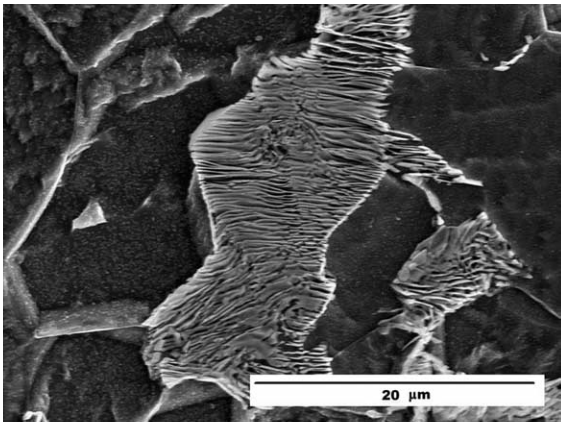

Fig. 2. Microstructure of modern hypoeutectoid steel (ASTM 1020), laminated under hot conditions and normalized. Thin interlamellar spacing of the pearlite structure can be observed.

Fig. 3. Microstructure of hypereutectoid steel (Acerinox), laminated under hot conditions and normalised. The grain limits filled with continous pro-eutectoid cementite as well as pearlite of thin interlamellar spacing inside the grains can be distinguished.

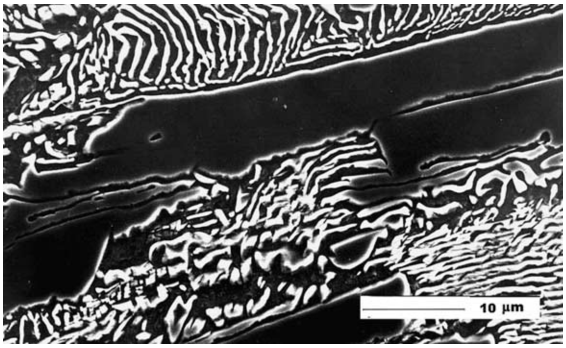

Fig. 4. Detail of Fig. 3, showing curved morphology of the pearlite cementite layers.

case of hypoeutectoid steels, the matrix consists of ferrite crystals (Fig. 2), while in hypereutectoid steel the grains are of pearlitic structure and their boundaries are filled with continuous pro-eutectoid cementite (Fig. 3). In spite of this, ageing processes are perceived in the cementite morphology, either eutectoid or pro-eutectoid. Very slow diffusion processes of carbon provoke these changes into the ferrite phase, slow because the solubility of carbon in ferrite is rather low, being 0.022 wt% at 720 °C and only 0.008 wt% at ambient temperature. This low solubility at room temperature, together with the tendency of iron carbide which appears in planar prismatic morphologies (idiomorphous), may be basically responsible for the geometrical changes observed. Nevertheless, it cannot be excluded that other phenomena, like surface tension or crystalline defect elimination, contribute in some way to the required energy for these structural changes.

The pearlite phase of antique steel samples, either hypo or hypereutectoid, shows a clear tendency towards prismatic idiomorphous cementite layers, with extensive planarity and parallel orientation, as can be seen in Figs. 5–8. Compared with the corresponding eutectoid cementite, it was observed that the cementite Widmanmstätten's needles type structure is of bigger shape and equally show planar and parallel layers (Fig. 8).

This idiomorphous behaviour and the orderly arrangement or fragmentation (fracture of lamellea) of the cementite of pearlite, which can be clearly distinguished in some colonies shown in Figs. 5 and 6, become the more evident the older is the investigated steel sample. Sometimes, as shown in Fig. 9, the pearlite colonies may present a rather irregular and clustered cementite structure, though the tendency for crystalline idiomorphism is evident. The different structure of pearlite

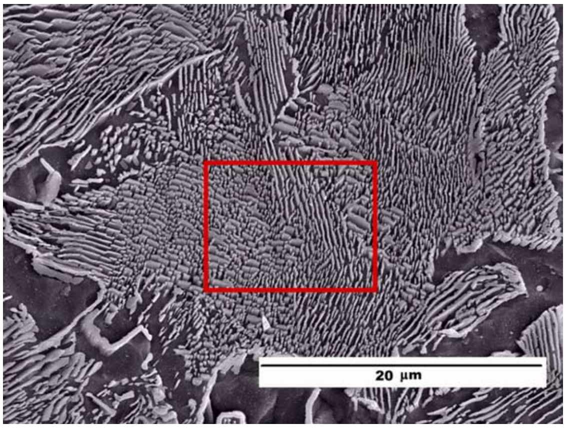

Fig. 5. Pearlite structure of hypoeutectoid steel proceeding from a Roman nail. (Cerro Muriano, Córdoba). The morphology is regular showing parallel ordered prismatic lamellae, the latter manifesting evident gradation or fragmentation.

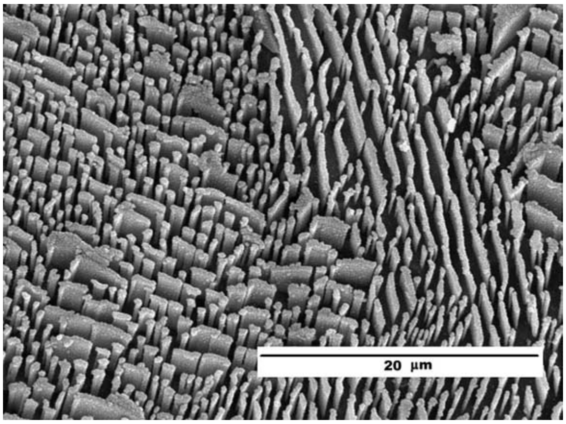

Fig. 6. Detail of Fig. 5, showing the generalised gradation or fragmentation of the cementite layers.

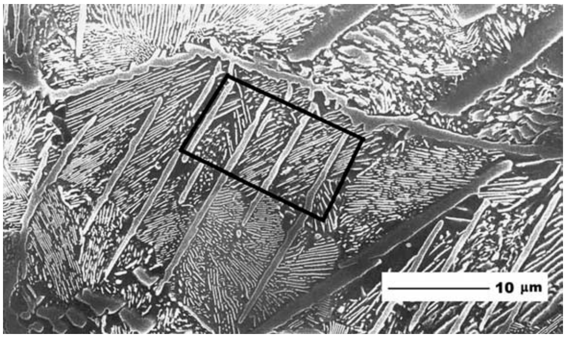

Fig. 7. Pearlite morphology of an hypoeutectoid steel, belonging to a 5th century (A.D.) Roman nail from the hermitage Santa Maria de Mijangos (Mijangos, Spain).

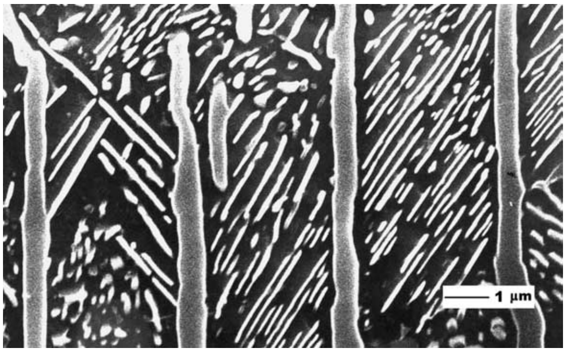

Fig. 8. Enlargement from Fig. 7. The parallelism and idiomorphism of the cementite layers of pearlite as well as of the needle of bigger-sized pro-eutectoid cementite type Widmanmstätten, can be clearly seen.

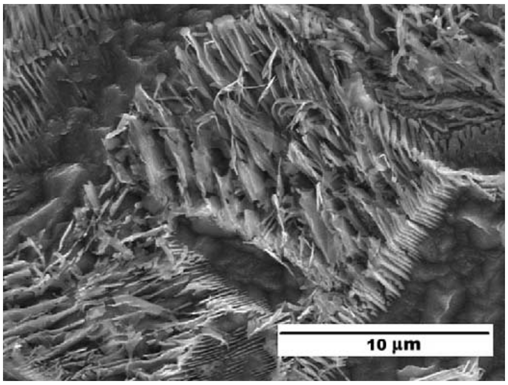

Fig. 9. Pearlite structure of Caliphal era nail, belonging to the roof structure of the Great Mosque of Córdoba. The prismatic layers of cementite are rather entangled.

colonies in older steel samples cause variations in the mechanical properties [8].

4. Conclusions

Ancient carbon steels that were hot-forged and cooled down at air (normalized process) show microstructure changes over the time. This is proved by studying different archaeologic samples of different chronology. Changes in the morphology, due to a very long and slow ageing process, during centuries and even millennia, demonstrate this. Possibly the most adequate indicator for these changes can be found in the cementite layers from pearlite colonies and equally, in the proeutectoid cementite in the case of hypereutectoid steel. The general tendency is towards an idiomorphism of planar prismatic shapes of very straight surfaces. The oldest structures evidently present a gradation or fragmentation of the cementite. The energy necessary for the diffusion and the maintenance of this process of microstructural evolution may derive from different sources, which have to be more deeply investigated.

In all the samples studied there is evidence for a microstructural evolution towards an ordered and regular geometry for both, eutectoid and pro-eutectoid cementite. These changes intrinsically cause variations in the mechanical properties of archaeologic steel compared with modern manufactured steels.

Ongoing studies focus on the quantification of these changes in terms of hardness, tensile strength or similar. Precise knowledge of these parameters could allow to estimate accurately the lifetime fulfilling previously established quality requirements of containers constructed with such material.

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